

PATENT SPECIFICATION

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(54) NEW METHYLOLGLYCIDYL ETHERS AND PROCESS FOR THEIR MANUFACTURE

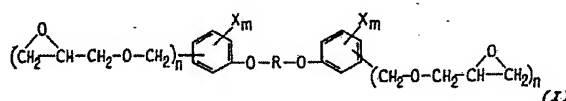
(71) We, CIBA-GEIGY AG, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Polynuclear phenols, such as bisphenol A and novolaks, are the most frequently employed intermediates for the epoxide resins normally used at present in industry. Carbonyl compounds, e.g. acetone, cyclohexanone, formaldehyde, glyoxal or acrolein, serve to effect the linkage of phenols with retention of the hydroxyl group. By etherification of this group with epichlorhydrin, in the presence of sodium hydroxide solution, are obtained the aforementioned synthetic resins. These do not, however, always possess after their curing, in the case of certain applications, satisfactory properties; in particular, when applied in the form of coatings subjected to severe mechanical stresses or to strong chemicals they often prove to be insufficiently resistant.

From the industry concerned with processing such products there is a continual demand, with regard to liquid epoxide resins based on bisphenol-A, for an ever increasing degree of purity and an ever lower viscosity. The result of this has been that the resins offered today often have a very high content of monomeric bisphenol-A-diglycidyl ether, and tend therefore to crystallise if stored at low temperature; and/or crystallisation is promoted by the addition of fillers, pigments, etc. It is now the aim to reduce this tendency of the resin to crystallise by the use of suitable additives. The requirement to be met in the case of an additive inhibiting crystallisation is that, whilst being fully effective in preventing crystallisation of the resin, it leaves all other properties of the resin as far as possible unaffected.

Surprisingly, certain epoxide resins containing phenol groups etherified with glycidyloxymethyl groups exhibit this property; and, at the same time, the use of the said epoxide resins enables products to be produced having better mechanical properties; furthermore, the obtained products are also chemically more resistant.

In one aspect the present invention consists in new epoxide resins of the formula:



wherein

R represents an alkylene or alkenylene group having a maximum mass of 2000 atomic weight units, and which can be interrupted by benzene nuclei and oxygen atoms as well as carry halogen- or oxygen-containing substituents,

X stands for an alkyl group having at most 12 carbon atoms, chlorine or bromine,

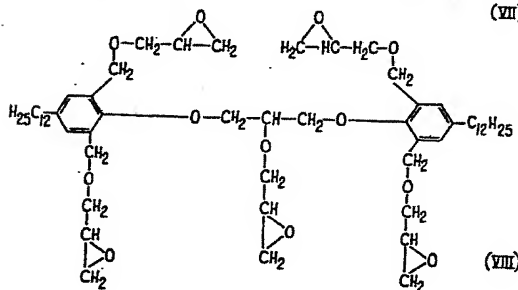
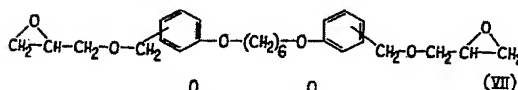
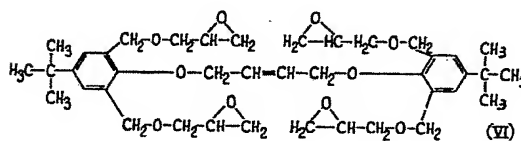
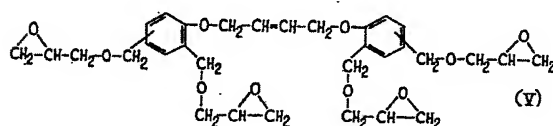
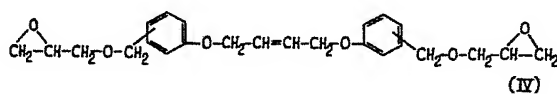
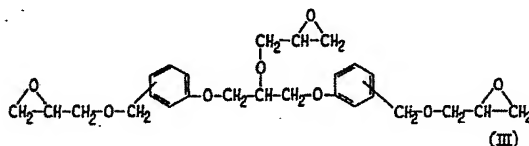
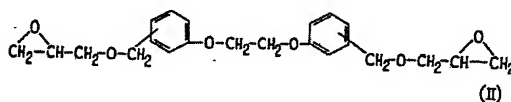
m stands for 0, 1 or 2, and

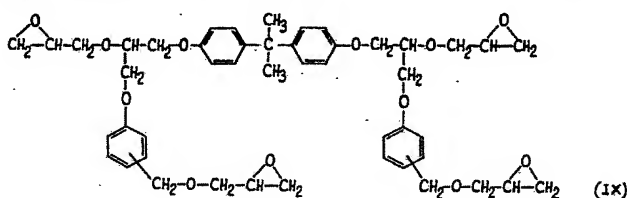
n stands for 1, 2 or 3.

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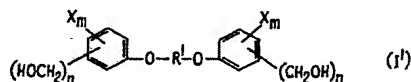
The compounds of formula I are viscous, liquid or low-melting solid resins yellow to brown in colour. A favourable feature distinguishing these compounds with regard to their processing is their negligible tendency to crystallise.

Preferred compounds of formula I are compounds in which R represents an alkylene or alkenylene group having 2 to 6 carbon atoms, or the 2-glycidyloxypropylene-1,3-group or the bisphenol-A-group, m stands for 0, and n stands for 1, 2 or 3. Examples of the new compounds are:





In another aspect the invention consists in the production of the new compounds by a process in which compounds of formula I':



wherein the group R' either has the meaning of R in formula I or stands for a group convertible into R by glycidylation with epichlorohydrin and elimination of hydrogen halide, and X, m and n have the same meanings as in formula I, are reacted with an epichlorohydrin with the elimination of the corresponding hydrogen halide. Preferably, 2 to 5 molecules of epichlorohydrin are used per hydroxyl group. Glycidylation is advantageously performed with azeotropic removal of the water in the presence of an HCl-acceptor, and optionally also in the presence of a catalyst. Suitable catalysts are quaternary ammonium halides, e.g. tetramethylammonium chloride, tetraethylammonium bromide, or benzyltrimethylammonium chloride.

Alkali metal hydroxides can serve as the HCl-acceptor: most simply NaOH in an equivalent amount or in a slight excess (up to 20%). Higher excess amounts lead to saponification of epichlorohydrin, and to contamination of the reaction product by polyglycerin. Advantageously, the sodium hydroxide solution is added as concentrated aqueous solution during the azeotropic removal of water under reduced pressure; water so added together with that formed during the reaction, is removed in this manner continuously from the reaction mixture. The sodium chloride formed during the reaction is subsequently either washed out or removed by centrifuging, and unreacted epichlorohydrin optionally distilled off *in vacuo*.

The starting compounds of formula I' can be obtained by reacting a phenol with 1—3 molecular proportions of formaldehyde in an alkaline medium, the reaction being performed carefully so as to avoid the formation of polycondensation products to the greatest possible extent. The obtained Na-hydroxymethylphenolates, or mixtures thereof, are reacted with an organic dihalogen compound having the radical R of the above given definition. Optionally, the radical R can be formed *in situ* from precursors. Suitable as radicals R are also epoxide, and particularly epichlorohydrin, radicals. Phenols usable in this process must have at least one free *ortho*- or *para*-position; advantageously, two (2,4 or 2,6) or even three (2,4,6) positions are unsubstituted. Examples of suitable phenols are phenol, *m*-cresol, *p*-*t*-butylphenol, nonylphenol, dodecylphenol, 2-chlorophenol and 2,4-dibromophenol. The formaldehyde is advantageously used in the form of a 30 or 37 per cent aqueous solution.

The alkali metal hydroxide best used is sodium hydroxide in concentrated aqueous solution. For the formation of the hydroxymethylphenol, it is sufficient in principle, to use enough to bring the pH to 8. For the subsequent reaction of the hydroxymethylphenol with the dihalogen compound, however, an equivalent amount of NaOH is necessary. The most simple procedure, therefore, is to add this amount when the formaldehyde addition is made. This reaction is best performed in the temperature range of 20 to 100°C, preferably at 60°C. If hydroxymethylation is incomplete, mixtures of position-isomeric hydroxymethyl compounds are generally obtained.

Examples of suitable reagents for the bridging of the hydroxymethylphenols are: 1,2-dibromoethane, 1,6-dichloro-*n*-hexane, 1,4-dichlorobutene-2, α,α' -dichloro-*p*- or *m*-xylene, α,α' -2,3,5,6-hexachloro-*p*- or *m*-xylene-2,2'-dichlorodiethyl ether, ethylene-glycol-di-2-chloroethylether, α,ω -Cl- or -Br terminated polyethylene or polypropylene oxides, glycerin-1,3-dichlorohydrin and epichlorohydrin.

For the "*in situ*" formation of the radical R, dihydric phenols are particularly suitable, such as resorcin, bisphenol A and its tetrabromine derivative, in combination with epichlorohydrin.

The mentioned dihalogen compounds can in many cases be reacted with aqueous solutions of hydroxymethyl-Na-phenolates, but for reasons of solubility, organic solvents, e.g. isopropanol or butanol are in some cases to be preferred.

The compounds of formula I can be converted into the insoluble and infusible state by the usual curing agents, e.g. carboxylic acid anhydrides, and compounds having several mobile hydrogen atoms, such as polyamines, polythiols, and polybasic acids, the conversion being optionally effected with the aid of heat. Anionic polymerisation catalysts, e.g. BF_3 and its complexes, or cationic polymerisation catalysts, e.g. tertiary amines, can be used to effect or accelerate the curing process. The compounds of the invention prove to be more reactive towards most of the known curing agents than those epoxides which are glycidyl ethers of polyvalent phenols (such as resorcinol, bisphenol A, and novolaks). The high reactivity of the compounds of the invention, combined with good flexibility, renders them particularly suitable as lacquer resins, casting resins, and dipping and impregnating resins. By virtue of their high reaction capacity, a high cross-linking density after curing can be obtained. For example, it is possible to produce, by curing with aliphatic or cycloaliphatic polyamines, coatings having excellent resistance to chemicals.

The polyvalency of many of the epoxide resins of the invention also renders possible curing with only bifunctional curing agents. Examples of such curing agents are primary monoamines such as butylamine, benzylamine or aniline, as well as compounds having two mercapto groups, such as ethanedithiol or 2,2'-dimercapto-diethyl ether. When such compounds are used with the diglycidyl ether of bisphenol A, for example only fusible soluble polyadducts are obtained.

To the epoxide resins can be added the usual additives such as active diluting agents for lowering the viscosity, extenders, fillers and toughening agents, also pigments, dyestuffs, softeners, flow control agents, thixotropic agents or fire-retarding materials. In yet another aspect therefore the invention consists in curable mixtures for the production of moulded articles which contain the polyglycidyl ethers of formula I and curing agents for epoxide resins, with or without one or more other epoxides and/or additives of the above mentioned types.

Specially for application in the lacquer field, the new polyglycidyl ethers can moreover be partially or completely esterified, in a known manner, with carboxylic acids, in particular with higher unsaturated fatty acids. It is also possible to add to such lacquer-resin compositions other curable synthetic resins, e.g. phenoplasts or aminoplasts.

The curable mixtures of the invention can be produced in the usual manner, with the aid of known mixing devices such as stirrers, kneaders and rollers.

The curable epoxide resin mixtures of the invention are useful, in particular, in the field of surface protection, in electrical engineering, for laminating processes, and in the building industry. They can be used in the form best suited for the purpose for which they are required, e.g. in the unfilled or filled state, optionally in the form of solutions or emulsions, as coating agents, lacquers, as (whirl-) sinter powders, moulding materials, injection-moulding compositions, dip resins, casting resins, impregnating resins, bonding agents and adhesives, as tool resins, laminating resins, sealing materials and fillers, floor-covering materials, and bonding agents for mineral aggregates. Their use for surface protection and for casting resins is particularly valuable.

The following Examples illustrate the invention. Except where otherwise stated, 'parts' and percentages are by weight. Parts by volume and parts by weight have the same ratio to each other as millimetre to gram.

Example 1.

Epoxide resin according to formula III

188 parts of phenol are mixed with 210 parts of 30% aqueous formaldehyde solution, and 84 parts of 50% aqueous sodium hydroxide solution are added dropwise as the mixture is stirred. As soon as the temperature of the reaction mixture has reached 50°C, it is maintained at this point by external cooling. Two hours after completion of the addition of sodium hydroxide solution, the reaction mixture is heated to 90°C and 102 parts of epichlorhydrin are added dropwise. In consequence of a slightly exothermic reaction, the reaction mixture commences to boil and becomes cloudy. It is allowed to gently boil for one hour with reflux-cooling and with stirring.

A further 1387 parts of epichlorhydrin are afterwards added; distillation is thereupon performed through a water-separator which allows the separation of the specifically lighter phase (water) and the return of the heavier phase (epichlorhydrin). During the azeotropic removal of the water, the pressure is gradually reduced until a boiling temperature of 55°C is established. 90 parts of water are separated and, with con-

tinuous azeotropic distillation at 50—55°C, additions are made dropwise of 15 parts of 50% aqueous tetramethylammonium chloride solution and 264 parts of 50% aqueous sodium hydroxide solution. On completion of the addition of sodium hydroxide solution, the water is removed completely (420 parts by volume) from the mixture, the sodium chloride which has separated out is removed by filtration, and the reaction solution washed with 100 parts by volume of an aqueous solution containing 10% of monosodium phosphate. The excess epichlorhydrin is afterwards distilled off in a rotary evaporator at 120°C and under 15 Torr; and the resin remaining is clarified by filtration, whilst still warm, over "Celite" (registered Trade Mark for a filter aid). In this manner are obtained, in quantitative yield, 478 parts of a medium-viscous, pale yellow resin characterised as follows:

	Found	Calculated
Epoxide content (equivalents per kilogram):	5.74	6.36
Chlorine content (%):	1.0	0
Content of saponifiable chlorine (%):	0.056	0
Mean molecular weight:	526	472
Viscosity at 25°C (cP):	8000	—
Colour number according to Gardner and Holdt:	4	—

The resin is particularly suitable as a non-crystallising casting resin and base resin for moulded articles, and also for the production of coatings resistant to chemicals.

Example 2.

Epoxide resin according to formula IV

940 Parts of phenol, 1100 parts of 30% aqueous formaldehyde solution and 800 parts of 50% aqueous sodium hydroxide solution are reacted, as described in the previous example, for 2 hours at 50°C. An addition is then made dropwise at 60°C, with stirring and external cooling, of 625 parts of 1,4-dichlorobutene-2; the reaction mixture is then allowed to react at this temperature for a further two hours. After cooling, a 3-phase system is obtained: oil phase, water phase and salt mass. The two lower phases are extracted twice with 925 parts of epichlorhydrin each time, and the extracts added to the oil phase; to this are then added a further 2775 parts of epichlorhydrin.

Water is removed from the resulting mixture by azeotropic distillation through a phase-separating vessel under reduced pressure with the boiling temperature at 55°C; additions are then made dropwise of 50 parts of a 50% aqueous solution of tetramethylammonium chloride and 880 parts of a 50% aqueous sodium hydroxide solution. After completion of the addition of sodium hydroxide solution, the azeotropic distillation is continued until the water is completely removed; the reaction solution is then cooled to room temperature, the precipitated sodium chloride filtered off, and the filtrate is washed with 200 parts of a 100% solution of monosodium phosphate in water. After the epichlorhydrin has been distilled off at 120°C/15 Torr in a rotary evaporator, there remain behind 1640 parts (79.6% of the theoretical amount) of a highly viscous, red-brown resin having the following characteristics:

	Found	Calculated
Epoxide content (equivalents per kilogram):	4.62	4.85
Chlorine content (%):	1.09	0
Amount of saponifiable chlorine (%):	0.06	0
Mean molecular weight:	432	412
Viscosity at 25°C (cP):	172,000	—
Colour number according to Gardner and Holdt:	12	—

The resin can be employed as described in Example 1.

Example 3.

Epoxide resin according to formula V

The procedure used is the same as that in Example 2, but instead of 1100 parts, 2000 parts of 30% aqueous formaldehyde solution are reacted with 940 parts of phenol and 800 parts of 50% aqueous sodium hydroxide solution.

After the reaction with dichlorobutene and with epichlorhydrin, 2295 parts (78.6% of the theoretical amount) of a yellow viscous resin are obtained having the following characteristics:

	Epoxide content (equivalents per kilogram):	<i>Found</i> 6.06	<i>Calculated</i> 6.85	
	Chlorine content (%):	1.1	0	
	Amount of saponifiable chlorine (%):	0.08	0	
5	Mean molecular weight:	613	584	5
	Viscosity at 25°C:	16400 cp	—	
	Colour number according to Gardner and Holdt:	5		

The resin can be employed as described in Example 1.

Example 4.

Epoxide resin according to formula VI

An amount of 300 parts of solid sodium hydroxide is dissolved in 5960 parts of water, and to this solution are then added, with stirring, 1125 parts of 4-*t*-butyl-phenol. An addition is made dropwise at 55—60°C, in the course of one hour, of 1237.5 parts of 37% aqueous formaldehyde solution; the whole is then allowed to react further for 1 hour at 60°C. During this period, the colour changes from the initial yellow-brown to orange and then to yellow-green. 468.75 parts of 1,4-dichlorobutene-2 are then added dropwise at 60°C in the course of 45 minutes, and the reaction is allowed to continue at this temperature for 6 hours, in the course of which large amounts of the crystallised intermediate product are formed. The reaction solution is cooled to room temperature, and the crystals are separated on the centrifuge, washed well with water and dried at 70°C *in vacuo*. In this way are obtained 1765 parts (99.7% of the theoretical amount) of the tetramethylol compound, M.P. 170—171°C.

118.5 parts of this intermediate product are dissolved at the boiling temperature in 925 parts of epichlorhydrin; to the solution are added 10 parts of a 50% aqueous solution of tetramethylammonium chloride, and the pressure is gradually reduced to the level where a boiling point of 80°C is established. With simultaneous azeotropic water-separation, 88 parts of 50% aqueous sodium hydroxide solution are added dropwise; the reaction mixture is freed from water, filtered, and washed with NaH₂PO₄ solution, and unreacted epichlorhydrin removed in a rotary evaporator at 120°C and 15 Torr. There is obtained in quantitative yield 174 parts of a highly viscous, clear, dark-red resin having the following characteristics:

	Epoxide content (equivalents per kilogram):	<i>Found</i> 4.53	<i>Calculated</i> 5.74	
	Chlorine content (%):	1.98	0	
	Amount of saponifiable chlorine (%):	0.23	0	
35	Mean molecular weight:	650	696	35
	Viscosity at 25°C:	144.000	—	
	Colour number according to Gardner and Holdt:	14		

The resin can be employed as described in Example 1.

Example 5.

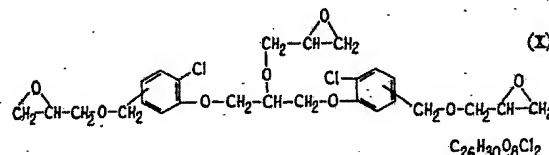
Epoxide resin according to formula VII

376 parts of phenol and 440 parts of 30% aqueous formaldehyde solution are mixed, and 320 parts of 50% sodium hydroxide solution are added dropwise. The temperature is allowed to rise to 60°C, and kept there for 2 hours. An addition is then made of 310 parts of 1,6-dichlorohexane, and the whole is heated to boiling for 20 hours. 1850 parts of epichlorhydrin are afterwards added, and 550 parts of water removed by azeotropic distillation at 90—95°C. The pressure is gradually reduced to 120 Torr, and in this manner a boiling temperature of 55—60°C established. With continuous distillation through the phase-separating vessel, 20 parts of a 50% aqueous solution of tetramethylammonium chloride are added dropwise, and then likewise 352 parts of 50% aqueous sodium hydroxide solution. After processing in the manner described in the preceding Examples, 177.1 parts of a resin are obtained having an epoxide content of 3.11 equivalents/kg, a viscosity of 140 cP at 25°C, and a colour number according to Gardner and Holdt of 4.

The resin can be employed in the manner described in Example 1.

Example 6.

Epoxide resin according to formula X:



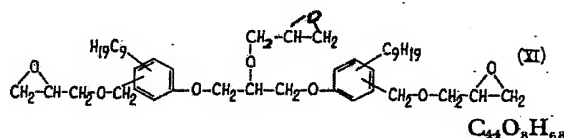
257 parts of O-chlorophenol are mixed with 210 parts of 30% aqueous formaldehyde solution, and to the mixture are added dropwise, with stirring, 84 parts of 50% aqueous sodium hydroxide solution. As soon as the reaction mixture has attained a temperature of 50°C, this temperature is maintained by external cooling. One hour after completion of the addition of sodium hydroxide solution, the temperature is raised quickly to 90°C by heating, and 102 parts of epichlorhydrin are added dropwise. The reaction mixture commences to boil in consequence of a slightly exothermic reaction. After the addition of epichlorhydrin has been made, the reaction mixture is allowed to gently boil, with reflux cooling and stirring, for a further hour.

A further 1387 parts of epichlorhydrin and 15 parts of 50% aqueous tetramethylammonium chloride solution are afterwards added; distillation is thereupon performed through a water-separator which allows the separation of the specifically lighter phase (water) and the return of the heavier phase (epichlorhydrin). The pressure is reduced to obtain for the azeotropic removal of water a boiling temperature of 50—55°C. After 30 minutes of circulation distillation, 187 parts by volume of water have been separated and, with continuous azeotropic distillation at 50—55°C boiling temperature, the addition is made dropwise, in the course of 2 hours, of 264 parts of 50% aqueous sodium hydroxide solution. After completion of the addition of sodium hydroxide solution, water is removed entirely from the mixture (total water separated: 367 parts by volume); the sodium chloride which has separated out is removed by filtration, and the filtrate washed with 100 parts by volume of a 10% aqueous monosodium phosphate solution. The unreacted epichlorhydrin is subsequently distilled off in a rotary evaporator at 120°C and 20 Torr, and the resin remaining behind is filtered, whilst still warm, through "Celite" to clarify it. In this manner are obtained 482 parts of a medium-viscous, light-brown resin having the following characteristics:

	Found	Calculated
Epoxide content (equiv./kg):	4.87	5.55
Chlorine content (%):	13.44	13.11
Content of saponifiable chlorine (%):	0.06	—
Viscosity at 25°C (cp):	43,800	—
Colour number according to Gardner and Holdt:	7	—

Example 7.

Epoxide resin according to the following structural formula (XI):



440 parts of nonylphenol, 210 parts of 30% aqueous formaldehyde solution and 84 parts of 50% aqueous sodium hydroxide solution are reacted, as described in Example 1, at a reaction temperature of 50°C. The reaction mixture is subsequently held for a further 3 hours at 50°C; the temperature is then raised to 90°C, and during a quarter of an hour an addition is made dropwise, with removal of the heating bath, of 102 parts of epichlorhydrin. The reaction mixture is then allowed to gently boil, with reflux cooling and stirring, for a further three quarters of an hour; a further 1387 parts of epichlorhydrin and 15 parts of an aqueous 50% tetramethylammonium chloride solution are thereupon added to the mixture.

With a boiling temperature of 50—55°C and during azeotropic distillation through a phase-separating vessel, as described in detail in the preceding Examples, 264 parts

of an aqueous 50% sodium hydroxide solution are added. The water is removed entirely from the mixture (total amount of water separated: 350 parts).

Subsequent processing as already described in the preceding Examples yielded 685 parts of medium-viscous resin having the following characteristics:

5		<i>Found</i>	<i>Calculated</i>	5
	Epoxide content (equiv./kg):	3.07	4.14	
	Chlorine content (%):	0.45	—	
	Content of saponifiable chlorine:	0.12	—	
	Viscosity at 25°C (cp):	38,800	—	
10	Colour number according to Gardner and Holdt:	5	—	10 ⁺

Example 8.

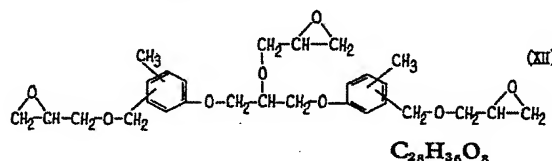
Epoxide resin according to formula (IX):

188 parts of phenol, 210 parts of 30% aqueous formaldehyde solution and 164 parts of 50% aqueous sodium hydroxide solution are reacted, as described in the preceding Examples, at a reaction temperature of 50°C. To the reaction mixture are then added 228 parts of bisphenol A; the reaction temperature is afterwards raised to 90°C, the heating bath is removed, and an addition is then made dropwise during one hour of 194 parts of epichlorhydrin. A slightly exothermic reaction results in the reaction mixture commencing to boil, and during the time of the dropwise addition it becomes increasingly more viscous. The reaction is allowed to continue for a further hour at 90°C; a further 1850 parts of epichlorhydrin are then added, and the water present is removed by azeotropic distillation at a boiling temperature of 50–55°C. With continuous distillation through a phase-separating vessel, additions are made dropwise, under constant conditions, of 20 parts of a 50% aqueous tetramethylammonium chloride solution, and then of 352 parts of a 50% aqueous sodium hydroxide solution. After processing as described in the preceding Examples, 812 parts of a highly viscous resin are obtained having the following characteristics:

		<i>Found</i>	<i>Calculated</i>	
	Epoxide content (equiv./kg):	4.12	4.92	
	Chlorine content (%):	0.4	—	
	Saponifiable chlorine (%):	0.164	—	
	Viscosity at 25°C (cp):	>100,000	—	
	Mean molecular weight:	871	—	
	Colour number according to Gardner and Holdt:	3	—	

Example 9.

Epoxide resin of the following structural formula (XII):



530 parts of a commercial mixture of cresol isomers are mixed with 450 parts of 30% aqueous formaldehyde solution. An addition is made dropwise, with stirring, of 200 parts of 50% aqueous sodium hydroxide solution, with external cooling to prevent the temperature of the reaction mixture exceeding 50°C. Stirring of the reaction mixture continues at room temperature over night; the mixture is subsequently heated to 60°C, and an addition is made dropwise at this temperature of 232 parts of epichlorhydrin. The reaction mixture is held, with continued stirring, for a further 2 hours at 60°C. A further 1525 parts of epichlorhydrin and 500 parts of water or 50–60°C are afterwards added; the whole is thoroughly stirred, and the lower organic phase separated in a separating funnel. After the addition of 13.3 parts of a 50% aqueous tetramethylammonium chloride solution at a boiling temperature of 50–55°C, and with azeotropic distillation through a phase-separating vessel, as described in detail in the preceding Examples, 480 parts of a 50% aqueous sodium hydroxide solution are added. The complete removal of water is then effected (total amount of water separated: 360 parts). The mode of processing already repeatedly described yielded 1017 parts of dark-brown viscous resin having the following characteristics:

	<i>Found</i>	<i>Calculated</i>	
Epoxide content (equiv./kg):	4.5	6.0	
Chlorine content (%):	0.4	—	
Content of saponifiable chlorine:	0.14	—	
5 Viscosity at 25°C:	262,000	—	5
Colour number (G + H):	13	—	

Coating tests

Application Example A

10 100 parts of the epoxide resin described in Example 1 are homogeneously mixed with 39 parts of a curing agent consisting of a phenol-accelerated adduct of trimethylhexamethylene diamine and a liquid epoxide resin based on bisphenol A and epichlorhydrin. This mixture has a viscosity at 25°C of ca. 6000 cP. Coatings produced with this mixture and having a dry film thickness of 160—180 μ display a light-yellow inherent colour. Coatings of this thickness require, at a temperature of 20°C and relative humidity 65%, about 4 hours to become fully cured. After 24 hours under these conditions, the pendulum hardness according to Persoz is 207", and, after one month at 15 20°C, the cupping value according to Erichsen is measured and found to be 5 mm. If the month's ageing is effected at 60°C, the Erichsen value is still 3 mm.

20 After ageing for 1 month at 20°C or for 1 month at 60°C, the value obtained in the impact test is 50 cm/kg. The mandrel-bending test with the 15 mm mandrel gives, with constant ageing times and curing temperatures, a value of 120° (angular).

Films formed in this way possess, after 10 days' curing at 20°C, resistance to hot water, dilute inorganic acids, aqueous neutral and alkaline solutions, as well as to aliphatic and aromatic hydrocarbons.

Application Example B

25 100 parts of the epoxide resin described in Example 6 are homogeneously mixed with 33 parts of the curing agent used in Example A. The viscosity of this mixture at 20°C is ca. 40,000 cP. If this mixture is applied with a dry film thickness of 160—180 μ , then it requires ca. 4 hours for complete curing at 20°C and relative humidity 30 65%. Under these conditions, the pendulum hardness after 24 hours is 165" (Persoz); and after one month the cupping-value (Erichsen) is 5 mm. After one month's ageing at 60°C, the Erichsen value is still 1 mm. In the impact test, a value of 60 cm/kg is obtained after an ageing treatment of 1 month at 20°C or 1 month at 60°C.

35 A film formed in this way possesses, after 10 days' curing at 20°C, resistance to hot water, dilute inorganic acids, aqueous neutral and alkaline solutions, as well as to aliphatic and aromatic hydrocarbons.

TABLE 1

Casting test.

The described methylolglycidyl ethers are well mixed with the amounts (given in the following table) of phthalic acid anhydride or with an adduct of 1 mole of triethylenetetramine and 2 moles of propylene oxide. The mixtures are poured into aluminium moulds (10×44×133 mm) and cured at 120°C and 40°C.

The properties of the cast specimens are shown in the following table:

Appl. Example	100 g of methyl- olglycidyl ether according to Example No.	g of amine curing agent per 100 g of methylol- glycidyl ether	Phthalic acid anhydride per 100 g of methyl- olglycidyl ether	Flexural strength VSM 77103 kg/mm ²	Impact strength VSM 77105 cmkg/cm ²	Mechanical dimen- sional stability in the heat according to Martens DIN 53 458 in °C	Water absorption after 1 hour 100°C (%)
C	1	11	74	13.4 13.3	4.8 9.1	80 57	0.60 2.1
D	2	17.4	57	6.4	4.8	45 flexible	0.44 1.92
E	3	18	67	17.0 13.8	6.9 6.8	62 47	0.48 3.30
F	4	too reactive	57	15.2	9.3	111	0.24
G	6	18.4	60	10.5 15.7	3.0 7.9	92 61	0.5 1.06
H	7	11.8	40	9.7	4.7 3.25	47 40	0.44 1.36
I	8		52	7.2	5.3	103	0.32
K	9	19.6	66	11.6 10.7	3.6 2.9	90 60	0.32 2.03

TABLE 2

Crystallisation tendency

Resin or resin mixture	Liquid bis-phenol-A-epoxide resin	L	M
Crystallisation time in days	3-5	>250	>250

TABLE 3

Curing with aliphatic polyamine

Resin or resin mixture	100 parts of liquid bis-phenol-A-epoxide resin	100 parts L	100 parts M
Triethylenetetramine	12.9 parts	13.5 parts	13.6 parts
Pot life at 40°C up to 3000 cP	20'	27'	19'
Curing	24h 40°	24h 40°	24h 40°
Impact strength (cm kg/cm ²)	21.3	21.4	34.8
Flexural strength	14.8	14.3	13.6
Deflection (mm)	8.3	7.4	8.6
Martens DIN (°C)	65	63	64
Tensile shearing strength on Anticorodal R (kg/mm ²)	0.21	0.48	0.36

TABLE 4

Curing with cycloaliphatic polyamine

Resin or resin mixture	100 parts of liquid bis-phenol-A-epoxide resin	100 parts L	100 parts M
Laromin C-260	31.8	33.0	36.0
Pot life at 40° up to 3000 cP	1h 01'	1h 30'	49'
Curing	24h 40°+6h 100°		
Impact strength (cm kg/cm ²)	29.8	18.9	28.3
Flexural strength (kg/mm ²)	15.1	13.5	15.0
Deflection (mm)	11.1	9.4	11.2
Martens DIN (°C)	109	103	108

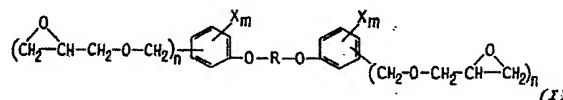
TABLE 5

Curing with hexahydrophthalic acid anhydride

Resin or resin mixture	100 parts of liquid bis-phenol-A-epoxide resin	100 parts L	100 parts M
Hexahydrophthalic acid anhydride 0.95 mol of anhydride per epoxide	77.5 parts	81 parts	82 parts
Tert. amine	1 part	1 part	1 part
Pot life at 80°C up to 1500 cP	1h 23'	1h 10'	1h 45'
Curing	4h 80°+6h 120°		
Impact strength (cm kg/cm ²)	14.1	18.3	19.2
Flexural strength (kg/mm ²)	15.1	15.0	15.8
Deflection (mm)	9.1	7.2	7.4
Martens DIN (°C)	118	104	112
H ₂ O-absorption after 4 days (R.T.) %	0.23	0.23	0.31
Loss-factor	tan δ >1% above	120°	105°
	tan δ >5% above	132°	122°
E _r at 25°C	3.5	3.5	3.7
Spec. insulation resistance at 25° (Ω-cm)	4•10 ¹⁶	9•10 ¹⁶	1•10 ¹⁷

WHAT WE CLAIM IS:—

1. New polyglycidyl ethers of the formula I:



5 wherein

R represents an alkylene or alkenylene group having a maximum mass of 2000 atomic weight units, and which can be interrupted by benzene nuclei and oxygen atoms as well as carry halogen- or oxygen-containing substituents,

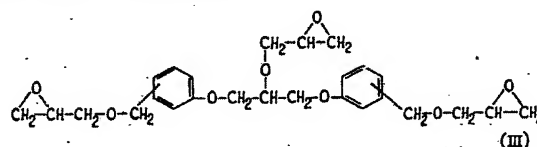
10 X stands for an alkyl group having at most 12 carbon atoms, chlorine or bromine, m stands for 0, 1 or 2, and n stands for 1, 2 or 3.

2. Polyglycidyl ethers according to Claim 1, in which R in formula I represents an alkylene or alkenylene group having 2 to 6 carbon atoms, and m stands for 0, and n for 1, 2 or 3.

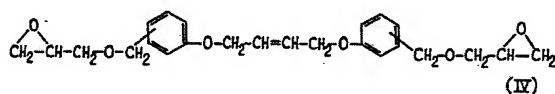
15 3. Polyglycidyl ethers according to Claim 1, in which R in formula I represents the glycidyl oxypropylene-1,3-group, and m stands for 0, and n for 1, 2 or 3.

4. Polyglycidyl ethers according to Claim 1, in which R in formula I represents the bisphenol-A group, m stands for 0, and n for 1, 2 or 3.

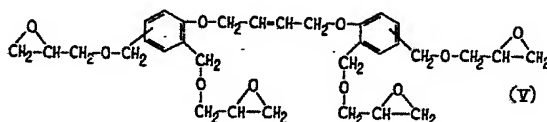
5. A polyglycidyl ether of the formula:



6. A polyglycidyl ether of the formula:

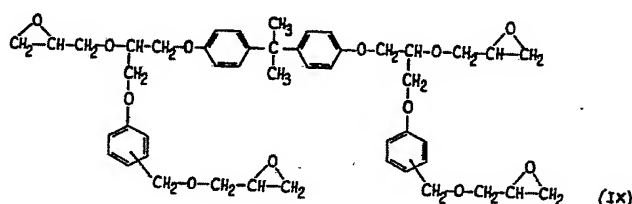


7. A polyglycidyl ether of the formula:



5

8. A polyglycidyl ether of the formula:



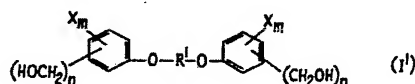
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9. Polyglycidyl ethers according to Claim 1 substantially as hereinbefore described.

10

10. Process for the production of new polyglycidyl ethers claimed in any one of Claims 1—9, in which a compound of formula:

10



wherein the group R' either has the meaning of R in Claim 1, or stands for a group convertible into R by glycidylation with an epihalogenhydrin and elimination of hydrogen halide, is reacted with an epihalogenhydrin with the elimination of the corresponding hydrogen halide.

15

11. Process according to Claim 10, in which the reaction is performed in the presence of an alkali metal hydroxide.

15

12. Process according to Claim 10 or 11, in which the water which is initially present in the reaction mixture, together with that formed in the reaction, is removed by azeotropic distillation from the reaction mixture.

20

13. Process according to one of Claims 10 to 12, in which 2 to 5 molecules of epichlorhydrin are used per OH-group of the hydroxymethylphenol ether of formula I'.

20

14. Process according to one of Claims 10 to 13, in which the reaction is performed in the presence of a catalyst.

25

15. Process for the production of polyglycidyl ethers according to Claim 10 substantially as hereinbefore described.

25

16. Curable mixtures for the production of moulded articles, which contain polyglycidyl ethers claimed in any one of Claims 1 to 9 and curing agents for epoxide resins.

30

17. Curable mixtures according to Claim 16, containing also epoxide resins based on bisphenol-A.

30

18. Curable mixtures according to Claim 16 substantially as hereinbefore described.

19. Moulded articles made from a mixture claimed in any one of Claims 16 to 18.

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